Studies of Mixed-metal Hydroxy-bridged Complexes. Part 1. Complexes with Bis(ethylenediamine)dihydroxocobalt(III) as Ligand

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Mixed-metal binuclear complexes are formed between $[Co(en)_2(OH)_2]^+$ (en = ethylenediamine) and divalent transition metal ions, with stability constants log K_1 = 7.2 (Cu); log β_2 = 5.9 (Mn), 7.5 (Co), 8.8 (Ni), 13.1 (Cu), 7.9 (Zn); at 25 °C, I = 3.0 mol dm^{-3} ($Na[ClO_4]$).

THE stabilities of hydroxide- or oxide-bridged polynuclear complexes have been extensively studied [1-5] and have been analysed theoretically,[6,7] yet very little is known of complexes involving two different metal ions. Some metal adducts of the VO_2^+ and NpO_2^+ ions [2] and of the $[Ru(NH_3)_5]^{2+}$ ion[8-10] have been characterised in solution, but otherwise very few stability constants for such systems have been reported. Labile binuclear complexes are postulated as intermediates in inner-sphere electron-transfer reactions and it is important to know their stabilities in order to evaluate rate parameters for the electron-transfer process. We have accordingly attempted to measure the interactions between the complex $[Co(en)_2(OH)_2]^+$ (en = ethylenediamine) and various metal ions, in order to estimate the stabilities of other analogous species. Evidence that the *cis*-$[Co(en)_2(OH)_2]^+$ unit can function as a chelate ligand comes from preparative chemistry. Werner obtained $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$ [11] and $[Co\{(OH)_2Co(en)_2\}_2]^{2+}$,[12] and Kobayashi *et al.*[13] have reported magnetic data for the latter, and for $[Ni\{(OH)_2Co(en)_2\}_2]^{2+}$. Hence in solution the equilibria (1) may be expected.

$$M^{m+} + n[Co(en)_2(OH_2)_2]^{3+} \rightleftharpoons [M\{(OH)_2Co(en)_2\}_n]^{(m+n)+} + 2nH^+ \qquad (1)$$

EXPERIMENTAL

Materials.—cis-*Diaquobis(ethylenediamine)cobalt*(III) *Nitrate*. *cis*-$[Co(en)_2Cl_2]Cl$ [14] was used to prepare $[Co(en)_2(CO_3)]Cl$ [15] and thence *cis*-$[Co(en)_2(OH)(OH_2)]Br_2$ [16] and the *cis*-diaquo-bromide [16] by published methods. The bromide was dissolved in the minimum volume of nitric acid (49.7% w/v) at −5 °C, and kept standing at this temperature with aeration to remove HBr and bromine. The product was precipitated by addition of two volumes of ethanol, washed with ethanol, and dried in air {Found: C, 12.3; H, 5.0; Co, 15.0; N, 24.7. $[Co(en)_2(OH_2)_2][NO_3]_3$ requires C, 12.0; H, 5.05; Co, 14.7; N, 24.5%}.

In a potentiometric titration, 1.015 ± 0.01 mol Na[OH] was required per mol of cobalt complex (1st end-point).

For titrations of the mixed-metal systems, carbonatobis(ethylenediamine)cobalt(III) chloride was dissolved in a slight excess of perchloric acid. Carbon dioxide was removed by bubbling nitrogen through the solution and excess acid was determined by titration with sodium hydroxide.

Solutions of $Mn[ClO_4]_2$ and $Zn[ClO_4]_2$ were prepared by dissolving the pure metals in perchloric acid; $Cu[ClO_4]_2 \cdot 6H_2O$ was prepared by dissolving freshly precipitated $Cu[OH]_2$ in perchloric acid and recrystallising the product. In all cases, the excess acid was determined by titration with Na[OH].

Titrations.—A Beckman Zeromatic pH meter was used, with glass and calomel electrodes and with a saturated NaCl salt bridge. The system was standardised with solutions of perchloric acid at ionic strength I = 3.0 mol dm^{-3} ($Na[ClO_4]$). The titration vessel was a stoppered double-walled beaker. Temperature was maintained at 25.0 ± 0.2 °C by circulating water from an external thermostat. Solutions were stirred by bubbling nitrogen.

RESULTS

Spectrophotometric Evidence of the Cobalt(III)–*Copper*(II) *Complex.*—Spectra of solutions of $[Co(en)_2(OH_2)_2]^{3+}$, Cu^{2+}, and of a 2 : 1 mixture of the two, all adjusted to the same pH, are shown in Figure 1. There is clear evidence of an interaction. Absorption due to Cu^{II} alone is negligible, but in the mixture the Co^{III} peak is shifted from 492 to 500 nm and

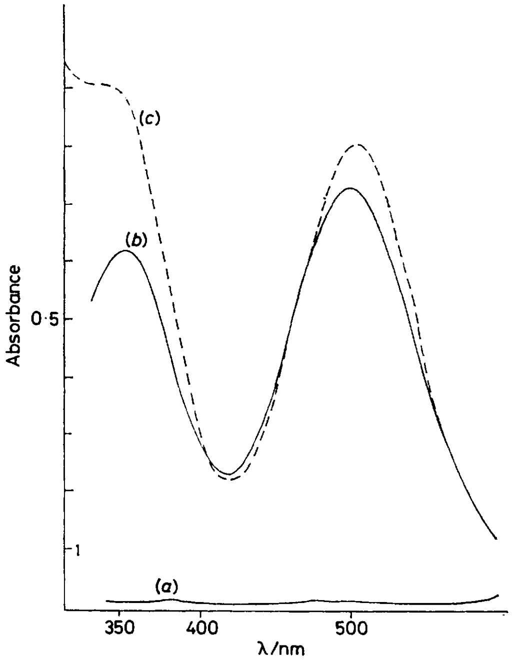

FIGURE 1 Absorption spectra of (*a*) $CuCl_2$ (0.005 mol dm^{-3}), (*b*) *cis*-$[Co(en)_2(OH_2)_2][NO_3]_3$ (0.010 mol dm^{-3}), and (*c*) the mixture $CuCl_2$ (0.005 mol dm^{-3}) and *cis*-$[Co(en)_2(OH_2)_2][NO_3]_3$ (0.010 mol dm^{-3}); all adjusted to pH 5.25 with added K[OH]. Temperature 25 °C, path length 1.0 cm

there is a large enhancement of absorbance in the u.v. range. A series of solutions was prepared with constant total concentration $a = [\mathrm{Co}]_T + [\mathrm{Cu}]_T$ and constant pH. Plots of ΔA against x, where $\Delta A = A - \frac{1}{2}(A_0 + A_1)$, A = absorbance, A_0 and A_1 are absorbances at $x = 0$ and $x = 1$ respectively, and $x = [\mathrm{Co}]_T/a$, are shown in Figure 2. The maxima occur close to $x = 0.67$, consistent with the formation of a Co_2Cu complex.[17]

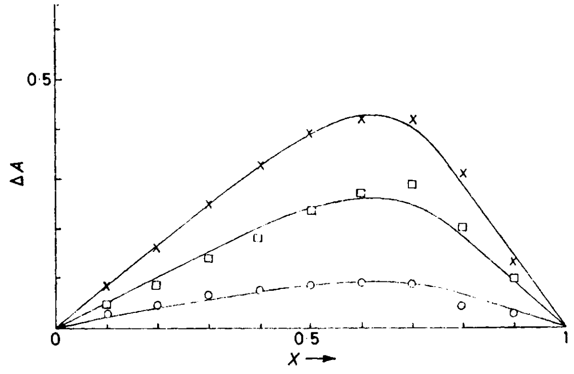

FIGURE 2 ' Job plots ' for mixtures of *cis*-$[Co(en)_2(OH_2)_2][NO_3]_3$ and $CuCl_2$; λ = 330 (×), 350 (□), 490 nm (○). $[\mathrm{Co}]_T = ax$, $[\mathrm{Cu}]_T = a(1 - x)$, $a = 0.010$ mol dm^{-3}, pH 4.5 (adjusted with Na[OH]), $I = 3.0$ mol dm^{-3} (Na[ClO$_4$]). Temperature 25 °C, path length 1 cm

Potentiometric Measurements.—From the pH-titration data, values of the acidity constants of the $[Co(en)_2(OH_2)_2]^{3+}$ ion were obtained by the method of Irving and Rossotti.[18] We define the equilibrium constants by the equations (2) and (3), where H_2L, HL, and L denote $[Co(en)_2(OH_2)_2]^{3+}$,

$$H_2L \rightleftharpoons HL + H^+ \qquad K_{a1} \qquad (2)$$

$$HL \rightleftharpoons L + H^+ \qquad K_{a2} \qquad (3)$$

$[Co(en)_2(OH)(OH_2)]^{2+}$, and $[Co(en)_2(OH)_2]^+$; and the function $\bar{n}_A$ by equations (4) and (5), where $[L]_F = [H_2L] +$

$$\bar{n}_A = (2[L]_F - B + [OH^-] - [H^+])/[L]_F \qquad (4)$$

$$\bar{n}_A = (K_{a1}^{-1}[H^+] + 2\,K_{a1}^{-1}K_{a2}^{-1}[H^+]^2)/(1 + K_{a1}^{-1}[H^+] + K_{a1}^{-1}K_{a2}^{-1}[H^+]^2) \qquad (5)$$

[HL] + [L], and B is the concentration of added alkali. Good constancy of pK_{a1} and pK_{a2} was obtained in the ranges $\bar{n}_A = 1.3$—1.7 and $\bar{n}_A = 0.3$—0.8, respectively. In the buffer region, the *cis–trans* equilibrium is established rapidly,[19] hence K_{a1} and K_{a2} are ' gross ' dissociation constants.[20] The values p$K_{a1} = 5.86 \pm 0.04$ and p$K_{a2} = 8.35 \pm 0.04$ at 25 °C, $I = 3.0$ mol dm^{-3} (Na[ClO$_4$]), may be compared with those reported by Bjerrum and Rasmussen,[20] 5.80 and 8.10, at 25 °C, $I = 1.0$ mol dm^{-3} (Na[NO$_3$]).

Titration curves for $[Co(en)_2(OH_2)_2]^{3+}$, and for the 2 : 1 mixture with Cu^{2+}, are compared in Figure 3. The lowering of pH in the mixture is consistent with complex formation [equation (1)]. There is no precipitation of Cu[OH]$_2$ until more than two equivalents of alkali per Cu ion have been added (pH 8.7), whereas on titration of Cu^{2+} in the absence of the cobalt complex the pH rises to *ca.* 6 with relatively small amounts of alkali, and Cu[OH]$_2$ is precipitated. Similar results were obtained with Ni^{2+}, Zn^{2+}, Co^{2+}, and Mn^{2+}, the pH-lowering diminishing in that order.

Assuming the equilibria (6)—(8), the Bjerrum formation

$$M + L \rightleftharpoons ML \qquad K_1 \qquad (6)$$

$$ML + L \rightleftharpoons ML_2 \qquad K_2 \qquad (7)$$

$$ML_2 + L \rightleftharpoons ML_3 \qquad K_3 \qquad (8)$$

$$\bar{n} = ([L]_T - [L]_F)/[M]_T \qquad (9)$$

number $\bar{n}$ is defined by equation (9) where $[L]_T = [L]_F + \Sigma[ML_i]$, and $[L]_F$ is defined above. Values of $\bar{n}$ were calculated by the method of Irving and Rossotti.[18] Choosing two points p and q, on the upper and lower curves of Figure 3, with the same pH, the value of $\bar{n}$ at point q is given by equation (10) where B_p and B_q are the concentrations of added alkali at points p and q, and n_{Ap} is the value of $\bar{n}_A$ at point p, calculated from equation (5).

$$\bar{n}_q = (B_q - B_p)/\bar{n}_{Ap}[M]_T \qquad (10)$$

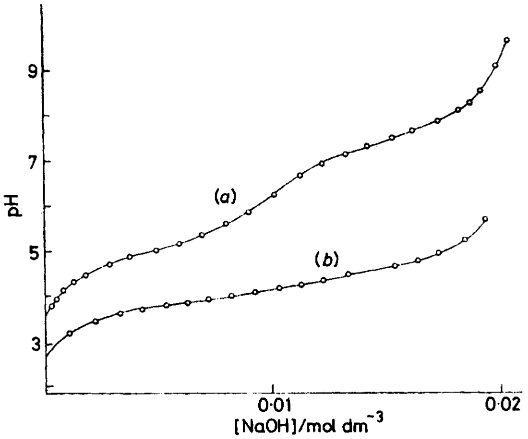

FIGURE 3 pH-Titration curves (*a*) for *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ (0.010 mol dm^{-3}), (*b*) for *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ (0.010 mol dm^{-3}) and Cu^{2+} (0.005 mol dm^{-3}), at 25 °C, $I = 3.0$ mol dm^{-3} (Na[ClO$_4$])

Results of titrations of the cobalt(III) complex with the metals Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, and Mn^{2+} are shown in Figure 4. For Cu^{2+}, titrations with Co : Cu ratios 3 : 1 and 2 : 1 were in fair agreement, the curves levelling off near $\bar{n} = 2$. For Ni^{2+}, with the same ratios, agreement was good up to $\bar{n}$ *ca.* 1.2, but at higher values of $\bar{n}$ the 2 : 1 curve

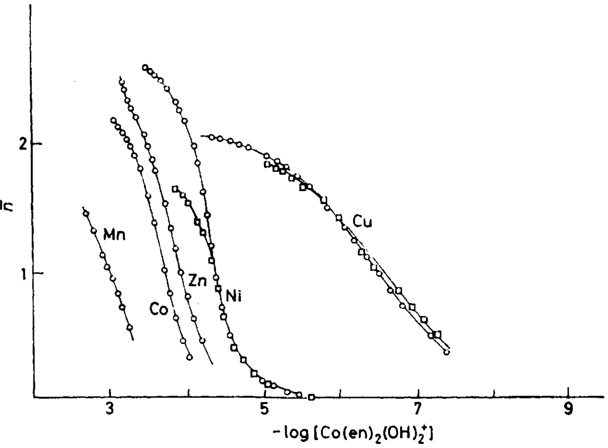

FIGURE 4 Formation curves for complexes $[M\{(OH)_2Co(en)_2\}_n]^{(m+n)+}$ at 25 °C, $I = 3.0$ mol dm^{-3} (Na[ClO$_4$]). $[Co^{III}]_T/[M^{II}]_T = 3.0$ (○); $[Co^{III}]_T/[M^{II}]_T = 2.0$ (□)

diverges. Precipitation was observed at the higher pH range of this system. For Zn^{2+}, titrations with Co : Zn ratios 4 : 1 and 3 : 1 were in good agreement. The curves extend above $\bar{n} = 2$ but do not reach $\bar{n} = 3$, owing to precipitation. For Co^{2+} and Mn^{2+}, ratios of 3 : 1 were used, but the formation curves were limited by precipitation at $\bar{n}$ *ca.* 2 and 1.4 respectively.

The data were fitted to the function (11), where $\beta_n =$

$$\bar{n} = \sum_{n=1}^{N} n\beta_n[\mathrm{L}]^n \Big/ \sum_{n=0}^{N} \beta_n[\mathrm{L}]^n \qquad (11)$$

$\prod_{n=1}^{N} K_n$, assuming $N = 2$ for the Cu^{2+} system and $N = 3$ for the other systems. Various graphical methods were employed, and comparison of the results obtained by different methods was used to judge the accuracy. Data for the Cu^{2+} system were treated by plotting $y = \bar{n}/(1 - \bar{n})[\mathrm{L}]$ against $x = (2 - \bar{n})[\mathrm{L}]/(1 - \bar{n})$. Satisfactory straight lines were obtained (*cf.* ref. 17, p. 94), giving the intercept $y = \beta_1$ where $x = 0$, and the slope β_2. For Ni^{2+}, plots of y against x in the range $\bar{n} = 0$—1.5 were used to obtain β_1 and β_2, and plots of $y' = (3 - \bar{n})[\mathrm{L}]/(\bar{n} - 2)$ against $x' = (\bar{n} - 1)[\mathrm{L}]/(\bar{n} - 2)$ in the range $\bar{n} = 1.5$—3 were used to obtain the intercept $y' = K_3^{-1}$ where $x' = 0$, and the slope $K_3^{-1}K_2^{-1}$. In both cases the slopes were well defined but the intercepts were small and ill defined. Least-squares fitting yielded $\beta_2 = K_1K_2 = (5.3 \pm 0.4) \times 10^8$ dm^6 mol^{-2}, $K_2K_3 = (1.5 \pm 0.1) \times 10^8$ dm^6 mol^{-2}, $K_1 = (2.1 \pm 3.0) \times 10^3$ dm^3 mol^{-1}, and $K_3 = (1.9 \pm 0.5) \times 10^4$ dm^3 mol^{-1}. We consider that only the first two parameters are experimentally significant: in other words our data do not justify fitting by more than two independent parameters. A plausible set of stepwise formation constants would be log $K_1 = 4.6$, log $K_2 = 4.2$, log $K_3 = 4.0$. For the other metals, plots of y against x were used to obtain β_1 and β_2 but again only the slopes were well defined. Least-squares fitting gave the following values of β_2: Mn $(0.96 \pm 0.02) \times 10^6$, Co $(3.03 \pm 0.04) \times 10^7$, Zn $(7.9 \pm 0.2) \times 10^7$ dm^6 mol^{-2}, while values of β_1 were small or negative: Mn $(0.6 \pm 0.1) \times 10^3$, Co $(-2.3 \pm 0.2) \times 10^3$, Zn $(-2.1 \pm 0.7) \times 10^3$ dm^3 mol^{-1}. These results imply that the 2 : 1 complex is predominant under the conditions of our experiments and, indeed, for all four metals, Mn, Co, Ni, Zn, we found that data in the range $n = 0$—1.5 could be represented almost equally well by equation (12) giving very similar values of

$$\bar{n} = 2\beta_2[\mathrm{L}]^2/(1 + \beta_2[\mathrm{L}]^2) \qquad (12)$$

β_2: Mn $(0.9 \pm 0.2) \times 10^6$, Co $(3.0 \pm 0.7) \times 10^7$, Ni $(6.2 \pm 1.0) \times 10^8$, Zn $(7.9 \pm 0.9) \times 10^7$ dm^6 mol^{-2} (averages and standard deviations of values calculated from each data point). On the basis of these calculations we propose the stability constants shown in the Table.

Equilibrium constants for the reactions $[Co(en)_2(OH)_2]^+$ with divalent transition-metal ions M^{2+}

M^{2+}	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
log K_1 [a]				7.2	
log β_2 [a]	5.9	7.5	8.8	13.1	7.9
pK_a^M [b]	10.7	10.6 [c]	9.9	8.4 [d]	9.1

[a] This work; 25 °C, $I = 3.0$ mol dm^{-3} (Na[ClO$_4$]). Limits of error in log K_1 are estimated to be ± 0.1. [b] $K_a^M = [M(OH)^{2+}][H^+]/[M^{2+}]$ (ref. 5, ch. 10); at 25 °C, $I = 0$. From data quoted on various transition-metal ions values of pK_a^M at $I = 1$—3 mol dm^{-3} are usually within ± 0.2 log unit of those at $I = 0$. Converted from molality to molarity using log K(molar) = log K(molal) − log 1.165 (ref. 5, p. 439). [c] Average of reported determinations at $I = 1.0$ mol dm^{-3} (Na[ClO$_4$]) and $I = 4.5$ mol dm^{-3} (Ba[ClO$_4$]$_2$). [d] Estimated from data on dilute solutions (ref. 5, p. 269) using ionic strength dependences reported for other divalent metal ions.

Like the pK_a values, the values of β_n relate to the equilibrium mixture of *cis* and *trans* cobalt complexes. For the equilibria (13) we have $\beta_n^c = \beta_n(1 + K_1^{-1})^n$ where K_1 is the

$$M^{2+} + n\ cis\text{-}[Co(en)_2(OH)_2]^+ \rightleftharpoons [M\{(OH)_2Co(en)_2\}_n]^{(2+n)+} \quad \beta_n^c \qquad (13)$$

[*cis*]/[*trans*] equilibrium constant for the bis(ethylenediamine)dihydroxocobalt(III) ions. Other workers have found $K_1 = 0.80$ at I 1.0 mol dm^{-3} (Na[NO$_3$] [20] or Na[ClO$_4$] [21]). If applicable to the present ionic medium this gives $K_1^c/K_1 = 2.25$, $\beta_2^c/\beta_2 = 5.1$.

DISCUSSION

For the copper(II) system, combining our data with the equilibrium constant for the reaction (14) gives log K_{CoCu}

$$Cu^{2+}(aq) \rightleftharpoons [Cu(OH)]^+ + H^+ \qquad K_{A1}^{Cu} \qquad (14)$$

$$[Co(en)_2(OH)(OH_2)]^{2+} + [Cu(OH)]^+ \rightleftharpoons [Co(en)_2(OH)_2Cu]^{3+} \qquad K_{CoCu} \qquad (15)$$

for (15), namely log K_{CoCu} = log K_1 − pK_{a2} + pK_{a1}^{Cu} = 7.2 − 8.35 + 8.4 * = 7.3. This may be compared with log K_{CuCu} *ca.* 5 (ref. 1) for the reaction (16). The higher stability of the Co–Cu complex relative

$$2[Cu(OH)]^+ \rightleftharpoons [Cu_2(OH)_2]^{2+} \qquad (16)$$

to the Cu–Cu complex presumably reflects a greater hydroxide-ion affinity of the cobalt centre, relative to the copper centre, as would be expected from the comparison of pK_a values of $[Co(en)_2(OH_2)_2]^{3+}$ and Cu^{2+}(aq) (5.9 and *ca.* 8.4* respectively).

The variation of β_2 for the five complexes Co^{III}–M^{II} also roughly parallels the values of pK_a^M (Table) but a more straightforward correlation is with the Irving-Williams sequence $Zn^{2+} < Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$. The marked peak in stability at M = Cu, with rather small differences in stability among the other members of the series, is in line with data for other bidentate oxygen-donor ligands, such as catechol.[2]

* See footnote *d* of Table.

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